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<b>(54) Title:</b> POROUS MEMBRANES OF INTERPENETRATING POLYMER NETWORKS  <b>(57) Abstract</b>  A porous polymeric membrane is soaked in a preparation of monomer(s) to give a swelled membrane. Polymerisation of the monomer to form an interpenetrating polymer network is then initiated.		

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POROUS MEMBRANES OF INTERPENETRATING  
POLYMER NETWORKS

FIELD OF THE INVENTION

This invention relates to porous interpenetrating polymer networks and methods of their manufacture.

BACKGROUND ART

5 Porous polymeric membranes are used for many filtration purposes. It is often desirable to modify the nature of the polymer from which the membrane is formed. For microfiltration, the membranes are often made of a polyolefin, such as polypropylene, chosen to withstand  
10 abrasion and vigorous chemical cleaning. Such polyolefins are hydrophobic and do not wet easily with aqueous feedstocks. Furthermore, they are not well adapted to modification by attachment of different chemical groupings.

15 Methods for reaction of materials such as polypropylene to form chemically modified polymers almost always involve chain breakage and consequent increased brittleness and reduced strength. Polypropylene which is especially desired as a membrane because of its physical properties is more easily destroyed by certain chemical treatments than other  
20 materials such as polyethylene. Direct chemical reaction of polypropylene may only be done in three ways: by free radical reaction, by anionic attack, or by cationic attack. These reactions usually employ extremely harsh and dangerous reagents, and generally cause at least some degradation of  
25 the polymer, with consequent deterioration of mechanical properties. This is particularly critical when dealing with the delicate structures present in filtration membranes.

For example, when sulfonating a block of polypropylene, damage to the surface 10 microns is not generally deleterious, but such damage, when sulfonating a membrane with wall thickness between the pores in the range of 0.1 to 10 microns, would totally destroy the material.

Attempts to solve the problem of membrane hydrophobicity and unsuitability to surface chemical modification have frequently involved treating the porous surface with various coating materials such as surfactants. It is however very difficult to find a material that will form an even, stable and chemically resistant film on the pore surfaces but that will not wear off after the membrane has been in use for an extended period. When these coating materials do wash off, not only are the properties of the membrane pore surfaces altered, but also the filtrate stream is contaminated.

Membranes may be formed into various shapes including flat sheets and hollow fibres. One form of filtration involves filtering aqueous feedstocks through porous hollow fibres. With time, solids in the feedstock deposit on the fibre, blocking the pores and slowing filtration. These blocking solids may be removed by gaseous backwash in which a gas such as air is blown in a direction opposite to that of the filtration path through the wall of the fibre. If a surfactant has been used in order to initially wet such a membrane, it will eventually wash off. When a gaseous

backwash is then applied to the membrane, the gas tends to dry the pores and return them to their native hydrophobic state, resulting in a marked reduction in flux.

There is therefore, a need for porous hollow fibres and other porous membrane structures that are water wettable and that are strong and resistant to chemical attack and totally insoluble in aqueous feed streams. There is also a need for porous membrane structures that have sites suitable for chemical modification and attachment of various chemical groupings, in order, for example, to confer ion exchange properties, or to enable attachment of biomolecules to the membrane.

The invention is based upon the formation of an interpenetrating polymer network of a second polymer in a preformed porous polymer matrix. This is known as a sequential interpenetrating polymer network. The invention may be applied to single porous hollow fibres or to bundles of such fibres, as well as to other membrane configurations. The sequential interpenetrating polymer network so formed is insoluble in any solvent and is crosslinked with negligible pore constriction. Furthermore, the interpenetrating polymer may be chosen to be capable of reaction so that surface chemical modification may be achieved.

The book "Interpenetrating Polymer Networks and Related Materials" by L.H. Sperling, Plenum Press 1981, states at page 3:-

"In its broadest definition, an interpenetrating polymer network, IPN, is any material containing two polymers, each in network form. A practical restriction requires that the two polymers have been synthesized and/or crosslinked in the immediate presence of each other. A sequential IPN begins with the synthesis of a crosslinked polymer I. Monomer II, plus its own crosslinker and initiator, are swollen into polymer I, and polymerised in situ."

An interpenetrating polymer network can be distinguished from simple polymer blends, blocks and grafts in two ways: (1) an interpenetrating polymer network swells, but does not dissolve in solvents, and (2) creep and flow are suppressed in an interpenetrating polymer network.

Polymers may be synthesized as linear, branched, or crosslinked entities, or a mixture containing all three. Crosslinks may be chemical or physical. Physical crosslinks arise from, amongst other causes, the crystalline portions of a semicrystalline polymer, giving the polymer rigidity and cohesivity. Such is the case with many polyolefins and with polyamides. A chemical crosslink may be defined as a covalent junction with a functionality greater than two, the chain segments of which generally extend to other crosslink sites, thus forming a network.

The theory of gelation defines a network as the point where the molecular weight becomes infinite. Such a polymer

is insoluble (but may be highly swellable), and technically consists of one macroscopic molecule. An interpenetrating polymer network thus consists of two polymers each crosslinked or otherwise connected within themselves in such a way as to form two entangled networks of polymers.

Many practical problems arise in the formation of sequential interpenetrating polymer networks using a porous polymer membrane with pores in the size range of 0.1 to 10 micrometres as the starting material. For example strong chemical conditions required for polymerisation of the introduced monomer can destroy the first polymer and incorrect procedures can lead to the pores being constricted by the second polymer. In addition, there are many practical problems in trying to sulfonate or attach other chemical derivatives to or on the walls of a porous polymer membrane. This is particularly so where the membrane must retain the physical properties of polypropylene. Many sulfonation methods are rapid and result in sulfonation mainly at the pore openings due to depletion of the reagent in the course of the reaction. A membrane typically has a pore length to diameter ratio of about 2000. It is thus very difficult to control conditions such that sulfonation occurs gently and evenly along the length of the pores and not exclusively at the opening to the pores.

It is an object of the present invention to provide a method of preparing a porous polymer membrane consisting of a sequential interpenetrating polymer network, which method may

be adapted to confer water wettable properties, strength and resistance to chemical attack to the membrane as well as being adapted to provide sites on the membrane suitable for chemical modification and attachment of various chemical groupings.

#### DISCLOSURE OF THE INVENTION

According to the invention there is provided a method of preparing a porous polymeric membrane consisting of an interpenetrating polymer network comprising the steps of:

- (a) soaking a porous polymeric membrane in a solution or vapour of a monomer that swells the polymer, said monomer being capable of delayed polymerisation, and,
- (b) initiating polymerisation of the monomer.

The invention also provides a method of preparing a porous polymeric membrane consisting of an interpenetrating polymer network comprising the steps of:

- (a) soaking a porous polymeric membrane in a solution of a monomer or mixture of monomers and a Lewis acid in a volatile solvent that inhibits polymerisation of the monomer(s), and
- (b) removing excess solution and solvent from the membrane thereby allowing polymerisation to occur.

The invention further provides a method of preparing a porous polymeric membrane consisting of an interpenetrating polymer network comprising the steps of:



- (a) soaking a porous polymeric membrane in a solution or vapour of a monomer or mixture of monomers in a volatile solvent, whereby said monomer(s) swells in the polymer,
- 5 (b) removing the solvent from the pores of the membrane, and,
- (c) reacting the treated membrane with a polymerising agent so as to polymerise the monomer.

In the specification and claims, the scope of the term "removing" is defined to include any means by which the solvent can leave the pores of the membrane to a degree sufficient that polymerisation of the monomer therein can occur. For instance, a membrane that is swelled by a monomer solution can have the solution that is not involved in the swelling displaced by a solution of polymerising agent which is forced through the membrane to a degree that will enable polymerisation of the monomer to occur.

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The preferred polymerising agent is a neat preparation or solution of any one of boron trifluoride gas, sulfuric acid, boron trifluoride etherate or sodium persulfate. In a preferred embodiment of the third method of the invention above, the removal of solvent described as step (b) is the result of treating the membrane with a polymerising agent. Suitable polymerising agents in this instance include aqueous sodium persulfate or boron trifluoride etherate in toluene, or sodium persulfate.

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In all the above embodiments of the invention, the preferred polymers are polyolefins such as propylene. Preferred monomers include divinylbenzene, styrene, a member of the styrene family, butadiene, or mixtures of these.

5       The solvent may be removed by heating, preferably to only a moderate temperature, or by blowing air or a gas over the surface, or by placing the treated membrane in a vacuum.

10       The inhibiting solvent may contain at least any one of the group comprising an ether, an alcohol, a solvent containing in its structure a lone pair of electrons on an oxygen, sulfur or nitrogen atom and an analogue of the solvent having the lone pair of electrons.

15       It is preferred that when divinylbenzene is loaded on a polypropylene membrane the divinylbenzene should be less than 40% based on the original weight of the membrane, otherwise the membrane may become very brittle. Loadings between 10% and 40% reduce the membrane's extension to break but increase the force to break.

20       It is preferred that the solvent is removed in such a way to avoid evaporation of monomer before crosslinking can take place. Preferably, the solvent is evaporated off in an oven with a low air flow rate.

25       The optimum temperature for removal of the solvent depends on the vapour pressure of the monomer, the vapour pressure of the ether or alcohol and the crosslinking rate.

      The preferred inhibiting component of the solvent is ether. The ether is preferably in a concentration in solvent

of from 5% to 10% volume/volume or the solvent may be ether itself. The preferred Lewis acid is boron trifluoride etherate.

5 The invention also provides porous membranes prepared by application of the above methods. The invention further provides porous polymer membranes consisting of sequentially prepared interpenetrating polymer networks.

10 The membranes that are the product of the above methods of the invention have strength and rigidity. The membranes so prepared may be reacted by conventional means with functionalizing agents to attach appropriate functional groups to the walls of the pores. Preferably the members are capable of sulfonation to give improved wettability and of further reaction to attach specific chemical groups to the surface groups as desired such as amine groups, sulphonyl  
15 chloride groups and carboxylate groups.

According to yet another aspect of this invention there is provided a method of preparing a porous polymer membrane consisting of an interpenetrating polymer network with  
20 sulfonate groups attached to the walls of the pores and optionally having other chemical groups attached to the sulfonate groups comprising the steps of:

- 25 (a) preparing a porous polymeric membrane consisting of an interpenetrating polymer network which does not have functional groups attached, by any one of the methods described above, and,

- (b) treating the membrane so prepared with a member of the group comprising a mixed anhydride of sulfuric acid and an organic acid, concentrated sulfuric acid or sulphonyl chloride or any functionalizing agent so as to attach sulfonate groups to the walls of the pores of the membrane, and,
- (c) optionally reacting the sulfonate group by conventional chemical means so as to attach other chemical groupings to the sulfonate groups.

Preferably, the organic acid moiety of the mixed anhydride of sulfuric acid and an organic acid is propanoic acid (which is also known as propionic acid) but others such as acetic acid or lauric acid may be used. When the organic acid moiety is either propanoic acid or lauric acid, the solvent used for dissolving the mixed anhydride is preferably dichloromethane.

The preferred method of treatment is to dissolve the mixed anhydride in the solvent, then place the membrane to be treated into the solution and allow it to soak at room temperature. The treated membrane is then removed, dried in air and washed with hot water.

Porous polymer membranes consisting of sequentially prepared interpenetrating polymer networks with sulfonate or other chemical groups attached to the walls of the pores are also provided by the invention.

Examples of chemical groupings that may be attached to the walls of the pores include electrophilic groups such as sulphonyl chloride groups and nucleophilic groups such as amine groups. Some typical reactions for attachment of groups are given in Fig. 1.

Further substitution of the aromatic portions of the polymer can be performed using any of the standard substitution reactions for aromatic substrates that can be applied to a microporous solid substrate. Examples of these reactions are chloromethylation, aminomethylation and nitration. These new functionalities can be further modified and used to introduce desired structures by standard organic chemical methods. For example, chloromethyl groups can be used to introduce molecules bearing amino groups by direct substitution. Many of these reactions are summarised in "Advanced Organic Chemistry: Reactions, Mechanisms and Structure," J. March, McGraw Hill Kogakusha, Tokyo 1968. Some examples are shown in Fig. 2.

In order that the invention may be more readily understood, reference will be made to the following examples. In the examples, the polypropylene fibres used were 0.6 mm outside diameter Accurel fibres from Membrana A.G. Divinyl benzene refers to a commercial mixture of ortho, meta and para isomers (about 55%) in a mixture of isomers of ethylvinyl benzene as supplied by Dow Chemicals.

Examples 1 to 11 illustrate different methods of producing membranes made of an interpenetrating polymer

network. In Examples 1 to 10 the extent of incorporation of the second network polymer was gauged by weight increase. In Example 1 and 9 a sample of treated fibre was burned to demonstrate the presence of poly (divinylbenzene) by the production of black sooty smoke. Examples 7, 8 and 9 also include the effects of the treatment on mechanical properties of the fibres.

Examples 12 to 14, 16 to 18, 20 and 21 illustrate methods of sulfonating the aromatic residues of the interpenetrating polymer network. Reaction in these cases was gauged either by wettability of the fibre or by staining with methylene blue, a cationic dye that binds to sulfonate groups. Example 21 includes the effects of the treatment on mechanical properties of the fibre, weight and flame property. The success of the sulfonation procedures confirms the success of the initial interpenetrating polymer network formation procedure, and is in some cases confirmed by the success of further elaboration procedures detailed in examples 15, 19 and 22.

#### EXAMPLE 1

A solution of divinylbenzene (25 ml) in ether (25 ml) was made up to 250 ml with freon 113. Boron trifluoride etherate (2.5 ml) was added and the resulting solution was mixed well. A bundle of 3000 polypropylene membrane fibres (25.100 g) was immersed slowly in this solution and soaked for 5 minutes. The bundle was then removed and dried at

60°C overnight. The weight per unit length was found to have increased from 0.61 mg/cm to 0.71 to 0.74 mg/cm (i.e. an increase of 16 to 21%). The fibres were found to burn with a smokey flame characteristic of aromatic materials.

5 EXAMPLE 2

To 10% divinylbenzene solution (as used in Example 1) in ether was added boron trifluoride etherate. The amount added was 1% based on the quantity of divinylbenzene solution. A bundle of 3000 polypropylene fibres (23.17 g), clamped  
10 tightly at one end only, was immersed slowly in the solution and then soaked for 5 minutes. The bundle was then removed from the solution, and nitrogen was blown down the lumens of the fibres at a sufficient pressure to clear the lumens of liquid. After drying overnight at 60° C, the bundle  
15 weighed 31.05 g (an increase of 32%).

EXAMPLE 3

A bundle of 3000 polypropylene membrane fibres (17.12g) was slowly immersed in a 10% solution of divinylbenzene in dichloromethane, and allowed to soak for 10 minutes. The  
20 bundle was then transferred to a vacuum vessel containing approximately 1 ml divinylbenzene and containing a mesh to prevent contact between the divinylbenzene and the bundle. A vacuum was applied for 2 minutes at room temperature and for a further 1 hour at 50°C. The vessel was sealed under  
25 vacuum, connected to a cylinder of boron trifluoride and the tap opened to admit the gas. After 5 minutes the vessel was re-evacuated and boron trifluoride readmitted. The bundle

was then allowed to react for 50 minutes at room temperature, then removed from the vessel and dried overnight at 60°C. The final weight of the bundle was 20.83g (i.e. an increase of 22%).

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EXAMPLE 4

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Boron trifluoride etherate (1.0 ml) was added to a solution of divinylbenzene (14.8 g) in methanol (150 ml). A bundle of 3000 polypropylene membrane fibres (13.17 g) was soaked in this solution for 1 hour and then dried at 60°C for three days. The final weight of the dried bundle was 19.20 g (i.e. an increase of 15%).

EXAMPLE 5

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Divinylbenzene (24.62 g) was made up to 250 ml with methanol, and then heated to 55°C. Water was added slowly until the solution went cloudy (46.7 ml). Methanol was then added until it went clear again (about 2ml) and the solution was then warmed to 60°C. A bundle of polypropylene membrane fibres (18.26g) was immersed slowly in the solution and soaked at 60°C for 45 minutes. The bundle was then removed from the solution, allowed to drain and then refrigerated (-10°C) for 10 minutes. It was then evacuated in a vacuum vessel to 20 mm Hg pressure for 5 minutes. Boron trifluoride gas was then admitted for 1 minute. The vessel was then re-evacuated and boron trifluoride gas readmitted. After 10 minutes, the bundle was removed from the vessel, boiled in acetone and dried at 60°C overnight. The final weight of the bundle was 19.73 g (i.e. an increase of 8%).



EXAMPLE 6

Solutions of 5, 10 and 20% (w/v) divinylbenzene in ether (10 ml) were prepared, each containing 10 drops of boron trifluoride etherate, and into each were immersed 5 preweighed fibres. These were soaked for 5 minutes and then dried at 60°C for 8 hours. These gave weight increases of 16, 23 and 107% respectively.

EXAMPLE 7

40 polypropylene fibres were soaked in a 5% solution of divinylbenzene in dichloromethane for 20 minutes. The solution was then removed, and the fibres heated at 65°C and 4kPa for 5 minutes in a vacuum vessel. The vessel was then flushed with boron trifluoride gas, re-evacuated and refilled with boron trifluoride gas. The fibres were then removed from the vessel and dried at 60°C. The fibres increased in weight through this procedure by 26%. A fibre was tested for extension properties. Results are shown in the Table 1 below.

TABLE 1

	Treated Fibres	Untreated Fibres
Elastic extension	15.6%	13.5 - 1.8%
Elastic limit	69g	43 - 3g
Break extension	160%	297 - 24%
Break force	87g	76 - 8g

EXAMPLE 8

Six 50cm lengths of polypropylene membrane fibre were soaked in a 5% (w/v) solution of divinylbenzene in methanol for 30 minutes. They were then transferred to a 7:3 mixture of sulfuric acid and water at 80 degrees centigrade. After soaking at this temperature for 30 minutes the fibres were washed thoroughly and dried. The test results which were obtained are shown in Table 2 below:

TABLE 2

	TREATED FIBRES	UNTREATED FIBRES
Break extension (%) (at 60% min. extension)	133	199
Break force (g-force) (at 60%/min. extension)	95	75
Water breakthrough pressure (kPa)	250	460
Weight per unit length	0.75	0.64

EXAMPLE 9

Ten 50 cm lengths of polypropylene membranes fibre were soaked in a 10% (w/v) solution of divinylbenzene in methanol for 30 minutes. Sodium persulphate (1.0g) was added to boiling water (200ml) and the drained fibres were immersed in the resulting solution immediately. Boiling was continued for 30 minutes, and the fibres were then removed and dried. The test results which were obtained (using the same test conditions as for Example 8) are shown in Table 3 below:

TABLE 3

Treated Fibres	
Break extension (%)	47
Break Force (g-force)	122
5 Water Breakthrough	50 kPa
Pressure (kPa)	
Weight increase (%)	8
Flame	Smokey Aromatic Flame

EXAMPLE 10

10 A PVDF membrane disc (Millipore HVHP 47mm diameter) was soaked in a solution of 2ml divinylbenzene in ether (20ml) to which 20 drops of boron trifluoride etherate had been added. After soaking for 20 minutes the disc was dried, boiled in alcohol and redried. The weight increase was 8%.

15 EXAMPLE 11

A 50cm polypropylene membrane fibre was soaked in 20% (v/v) divinylbenzene in toluene for 20 minutes and then a 20% (v/v) solution of boron trifluoride etherate in toluene was forced through the pores from the lumen side. The fibre was  
20 dried in air at room temperature for 10 minutes and then at 70 degrees centigrade for a further 20 minutes. Evidence that polymerisation of monomer occurred in this Example is found in Example 21, where the abovetreated fibres were sulfonated.

EXAMPLE 12

An interpenetrating polymer network membrane fibre produced as in Example 1 was soaked in a freshly prepared solution of sulfur trioxide (freshly distilled fromn oleum) in carbon tetrachloride (10% w/v). The fibre went a deep red colour which faded on removal from the solution. It was then washed in water and dried at 60°C. The surface of the fibre was found to wet with a dilute aqueous solution of methylene blue dye.

EXAMPLE 13

An interpenetrating polymer network membrane fibre (bubble point greater than 2 atmospheres) produced as in Example 1 was soaked in a freshly prepared solution of chlorosulfonic acid in dichloromethane (10% w/v; 5.6% v/v) for 15 minutes. The fibre turned red, but faded on immersion in 50% aqueous ethanol. The fibre was dried and was shown to wet with water at pressures greater than 1 atmosphere.

EXAMPLE 14

Ten interpenetrating polymer network membrane fibres (449.44mg) produced as in Example 1 were soaked overnight in a solution of lauroyl sulfate in cyclohexane (produced by reaction of a solution of 3g lauric acid in 10 ml cyclohexane with 1.5g chlorosulfonic acid). They were then washed in boiling acetone and extracted extensively with tetrahydrofuran. The dried fibres showed a weight gain of 73.05 mg. The theoretical value based on known incorporation of aromatic groups is 76.34 mg.

EXAMPLE 15

Five sulfonated membranes produced as in Example 14 were soaked in thionyl chloride for 1 1/2 hours. Extensive bubble formation ensued indicating reaction of the membrane. The fibres were removed and dried under vacuum ( 200 mTorr). They were then transferred to a solution of 10% JEFFAMINE M1000 (Texaco: amino terminated polyoxyethylene) in tetrahydrofuran and allowed to soak overnight. After washing and drying this membrane was found to pass water at trans-membrane pressure of about 1 atmosphere, whereas the base interpenetrating polymer network did not do so.

A sample of the sulfochlorinated membrane, prepared as described above, was immersed in an acetone solution of 4-aminoazobenzene (an azo dye). It was then boiled in acetone to remove unbound dye. The fibre dyed a uniform red colour, indicating even sulfochlorination throughout the fibre.

EXAMPLE 16

Ten interpenetrating polymer network membrane fibres, produced as in Example 1, were heated at 65°C in concentrated sulfuric acid for 3 days. The fibres turned purple, but faded on immersion in water. The fibres were boiled in water and dried at 60°C. They were then mounted in a 30 cm long glass cartridge and pressurised with water to 200 kPa. They were observed to swell in water, and at 100 kPa trans membrane pressure the fibres passed 11.0 ml water per minute, reducing the turbidity of the water from 1.6 NTU to 0.11 NTU. A dilute solution of methylene blue dye was

dried under vacuum for two hours at 20 mm Hg pressure and then soaked in a solution of 1,6-diaminohexane in tetrahydrofuran for 1 1/2 hours. They were then boiled in water several times and dried at 60°C. They were then  
5 soaked in aqueous p-nitrobenzenediazonium tetrafluoroborate for 10 minutes, washed well with water and then with acetone. This last procedure stained the membrane yellow-brown, indicating the presence of membrane-bound amino groups.

#### EXAMPLE 20

10 Sulphuric acid (2.0g) was treated dropwise with propionic anhydride (2.7g) and the resultant viscous liquid was dissolved in dichloroethane (20ml). The treated membrane disc produced in Example 10 was soaked in this solution for 2  
15 hours, and then washed in hot water, alcohol and then dried at 70 degrees centigrade. The resulting disc stained with methylene blue dye (indicating the presence of anionic surface groups) whereas an untreated disc from the same batch did not stain. Also the disc had a water flow rate of 72ml/4  
20 mins. under mild vacuum, whereas the untreated disc under identical conditions would not permit passage of water.

#### EXAMPLE 21

The fibres produced in Example 11 were slowly immersed in the sulfonating solution described in Example 20 and soaked for one and a half hours. After washing and drying,  
25 the test results which were obtained under the same test conditions as in Example 8 are shown in Table 4 below:

TABLE 4

	Treated Fibres
Break Extension	76%
Break Force	94 g-force
Water Breakthrough Pressure	300 kPa
Weight Per Unit Length	0.72 mg/cm
Methylene Blue Dye	Stained
Flame	Slightly Smokey Flame

EXAMPLE 22

20 ml sulfochlorinated interpenetrating polymer network membrane fibres produced as in Example 15 were soaked for 2 hours in a 5% solution of p-aminobenzoic acid in tetrahydrofuran. They were then extensively extracted with acetone and dried. A monoclonal antibody of human chorionic gonadotrophin was attached via the carboxylate group on the membrane using standard techniques and tested for binding with  $^{125}$ I-hCG (antigen). Binding was between 2 and 4 times that of an untreated membrane. The results are shown in Table 5.

then passed through the fibres, after which the cartridge was dismantled and the fibres were removed. They had stained evenly throughout. Unmodified interpenetrating polymer network membranes did not stain under similar conditions.

5 EXAMPLE 17

A 10% solution of acetyl sulfate in tetrahydrofuran was prepared from acetic anhydride and sulfuric acid. An interpenetrating polymer network membrane fibre prepared as in Example 1 was soaked in this solution. The resulting fibre was boiled in water and dried at 65°C. This fibre was shown to swell by 1.8% of its length on soaking in water.

10 EXAMPLE 18

Several interpenetrating polymer network membrane fibres (8.2g) were immersed in a solution (160 ml) of propionoyl sulfate (produced from 10.2 g sulfuric acid and 13.5g propionic anhydride) in dichloromethane. The fibres were soaked overnight, then washed repeatedly in hot water and dried. Ten fibres were then mounted in a 30 cm crossflow cartridge, and had a bubble point of 180 kPa. They passed water, without prior wetting, at 55ml per minute. Fibres prepared in this fashion stained well with methylene blue solution and were found to have an ion exchange capacity of 0.4 milliequivalents (meq) per gram.

15 EXAMPLE 19

25 Ten sulfonated interpenetrating polymer network membrane fibres produced as in Example 18 were treated with 10% thionyl chloride in dichloromethane for 1 1/3 hours,



TABLE 5

$^{125}\text{I-hCG}$		
Experiment	Total counts	Bound counts
1 Fibre 1 (coated)	66,000	61,000
5      Fibre 2 (control)	61,000	12,000
2 Fibre 1 (coated)	41,500	35,915
Fibre 2 (control)	40,000	15,993

The non-specific binding is rather high but attempts were not made to minimise this background.

10      Various modifications may be made in the methods of preparing the porous polymer membranes without departing from the scope and ambit of the invention.

CLAIMS

1. A method of preparing a porous polymeric membrane consisting of an interpenetrating polymeric network comprising the steps of:-

- (a) soaking a porous polymer membrane in a solution or vapour of a monomer that swells the polymer, said monomer being capable of delayed polymerisation, and
- (b) initiating polymerisation of the monomer.

2. A method of preparing a porous polymeric membrane consisting of an interpenetrating polymer network comprising the steps of:-

- (a) soaking a porous polymeric membrane in a solution or vapour of a monomer or mixture of monomers and a Lewis acid in a volatile solvent that inhibits polymerisation of the monomer(s), and,
- (b) removing excess solution and solvent from the membrane thereby allowing polymerisation to occur.

3. A method of preparing a porous polymeric membrane consisting of an interpenetrating polymer network comprising the steps of:-

- (a) soaking a porous polymeric membrane in a solution or vapour of a monomer or mixture of monomers in a volatile solvent, whereby said monomer(s) swells in the polymer,
- (b) removing the solvent from the pores of the

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comprising an ether, an alcohol, a solvent containing in its structure a lone pair of electrons on an oxygen, sulfur or nitrogen atom and an analogue of the solvent having the lone pair of electrons.

12. A method according to any one of claims 1 to 11 wherein the polymer is a polyolefin.

13. A method according to any one of claims 1 to 12 wherein the monomer is selected from the group consisting of divinylbenzene, styrene, any member of the styrene family, butadiene or mixtures of these.

14. A method according to any one of claims 1 to 13 wherein the polymer is polypropylene and the monomer is divinylbenzene loaded on the polypropylene membrane at less than 40% based on the original weight of the polypropylene membrane.

15. A method according to claim 14 wherein the divinyl benzene is loaded on the polypropylene membrane at between 10% and 40% based on the original weight of the polypropylene membrane.

16. A method according to claim 2 or any one of claims 11 to 15 when dependent on claim 2 wherein the inhibiting component of the solvent is ether.

17. A method according to claim 16 wherein the ether is in a concentration of between 5% and 10% volume/volume.

18. A method according to claim 2 or any one of claims 11 to 17 when dependent on claim 2, wherein the Lewis acid is boron trifluoride etherate.

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19. A porous polymer membrane consisting of a sequentially prepared interpenetrating polymer network.

20. A porous polymer membrane consisting of an interpenetrating polymer network whenever prepared by a method of any one of claims 1 to 18.

21. A method of preparing a porous polymer membrane consisting of an interpenetrating polymer network with functional groups attached to the walls of pores comprising the steps of:-

- (a) preparing a porous polymeric membrane by a method of any one of claims 1 to 18, and
- (b) treating the membrane so prepared with a functionalizing agent.

22. A method according to claim 21 wherein the functionalizing agent attaches sulfonate groups to the walls of the pores.

23. A method according to claim 21 or claim 22 wherein the functionalizing agent is a member of the group consisting of a mixed anhydride of sulfuric acid and an organic acid, chlorosulfonic acid, concentrated sulfuric acid or sulfuryl chloride.

24. A method according to claim 23 wherein the organic acid moiety of the mixed anhydride of sulfuric acid and an organic acid is selected from the group consisting of propanoic acid, acetic acid and lauric acid.

25. A method according to claim 24 wherein, when the said acid moiety is either propanoic acid or lauric acid, the mixed anhydride of sulfuric acid and an organic acid is dissolved in dichloromethane.

26. A method of preparing a porous polymer membrane consisting of an interpenetrating polymer network with sulfonate groups attached to the walls of the pores comprising the steps of:-

- (a) preparing a porous polymeric membrane by the method of any one of claims 1 to 18,
- (b) immersing the membrane so prepared into a solution of an anhydride selected from the group consisting of a mixed anhydride of sulfuric acid and an organic acid, concentrated sulfuric acid or sulfuryl chloride, to allow the membrane to soak at room temperature,
- (c) removing the soaked membrane and drying it in air, and
- (d) washing the membrane with hot water.

27. A method of preparing a porous polymeric membrane consisting of an interpenetrating polymer network with sulfonate groups attached to the walls of the pores and other chemical groups attached to the sulfonate groups comprising the steps of:-

- (a) preparing a porous polymer membrane by the method of any one of claims 22 to 26;

membrane, and

- (c) reacting the treated membrane with a polymerising agent so as to polymerise the monomer.

4. A method according to claim 3 wherein the polymerising agent is a neat preparation or solution of any one of boron trifluoride gas, sulfuric acid, boron trifluoride etherate, or sodium persulfate.

5. A method according to claim 3 or claim 4 wherein the solvent is removed by heating.

6. A method according to claim 3 or claim 4 wherein the solvent is removed by blowing air or a gas through the pores of the treated membrane.

7. A method according to claim 3 or claim 4 wherein the solvent is removed by placing the treated membrane in a vacuum.

8. A method according to any one of claims 2 to 7 wherein the solvent is removed in such a way to avoid evaporation of monomer before crosslinking can take place.

9. A method according to claim 3 wherein the removal of solvent described in step (b) is the result of treating the membrane with a polymerising agent in accordance with step (c).

10. A method according to claim 9 wherein the polymerising agent is aqueous sodium persulphate or boron trifluoride etherate in toluene.

11. A method according to claim 2 or claim 8 wherein the volatile solvent contains at least any one of the group

- (b) reacting the membrane so prepared by conventional chemical means so as to attach other chemical groups to the sulfonate groups.

28. A porous polymer membrane consisting of sequentially prepared interpenetrating polymer networks with sulfonate groups attached to the walls of the pores.

29. A porous polymer membrane consisting of interpenetrating polymer networks with sulfonate groups attached to the walls of the pores whenever prepared by a method of any one of claims 22 to 26.

30. A porous polymer membrane consisting of sequentially prepared interpenetrating polymer networks with sulfonate groups attached to the walls of the pores and other chemical groups attached to the sulfonate groups.

31. A porous polymer membrane consisting of interpenetrating polymer networks with sulfonate groups attached to the walls of the pores and other chemical groups attached to the sulfonate groups whenever prepared by a method of claim 27.

32. A method of preparing a porous polymer membrane consisting of interpenetrating polymer networks, said method being substantially as hereinbefore described with reference to any one of Examples 1 to 11.

33. A method of preparing a porous polymer membrane consisting of interpenetrating polymer networks with

sulfonate groups attached to the walls of the pores, said method being substantially as hereinbefore described with reference to any one of Examples 12 to 14, 16 to 18, 20 and 21.

34. A method of preparing a porous polymer membrane consisting of interpenetrating polymer networks with sulfonate groups attached to the walls of the pores and other chemical groups attached to the sulfonate groups, said method being substantially as hereinbefore described with reference to Examples 15, 19 and 22.

35. A porous polymer membrane consisting of sequentially prepared interpenetrating polymer networks with functional groups attached to the walls of the pores of the membrane.

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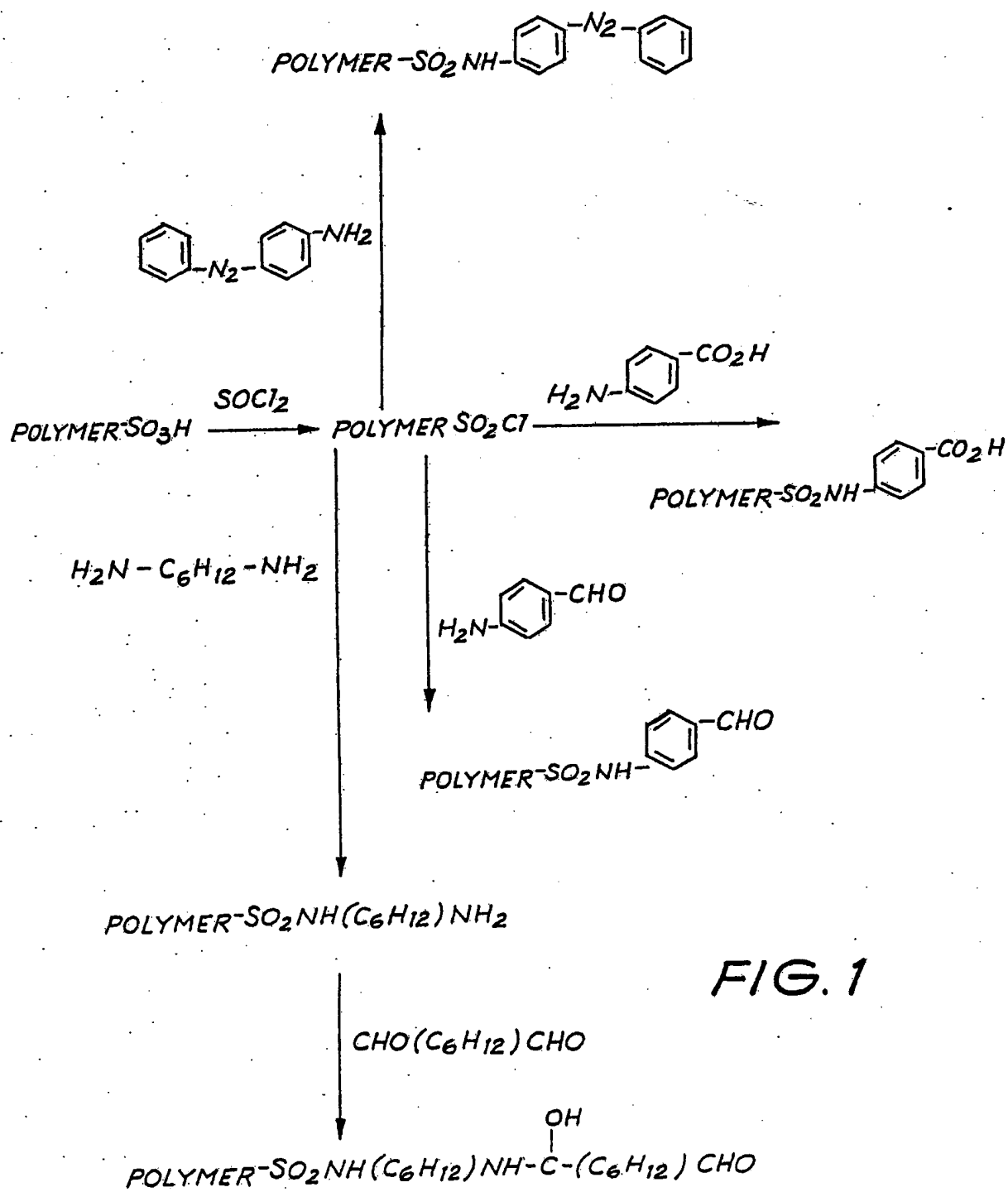


FIG. 1

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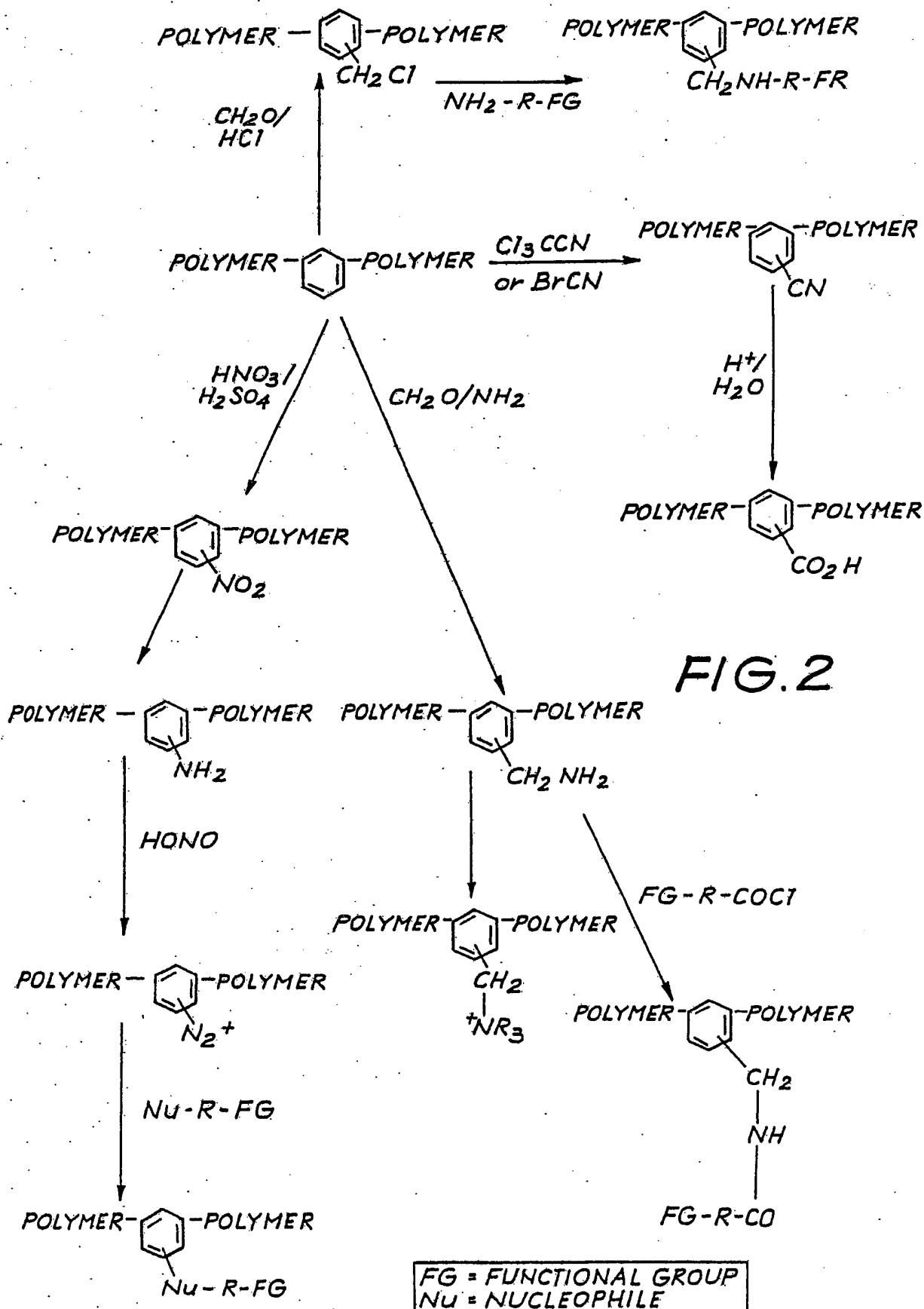


FIG.2

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/AU 88/00256

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) According to International Patent Classification (IPC) or to both National Classification and IPC <div style="text-align: center; font-family: monospace;">Int. Cl.<sup>4</sup>    C08J 7/16, 5/22, B01D 13/04</div>						
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; font-size: small;">Minimum Documentation Searched<sup>1</sup></div> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;">Classification System</td> <td style="width: 50%; border: none;">Classification Symbols</td> </tr> <tr> <td style="border: none; text-align: center; padding: 10px 0;">IPC</td> <td style="border: none; text-align: center; padding: 10px 0;">C08J 7/16, 5/22</td> </tr> </table> <div style="text-align: center; font-size: x-small; margin-top: 5px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched<sup>2</sup></div>			Classification System	Classification Symbols	IPC	C08J 7/16, 5/22
Classification System	Classification Symbols					
IPC	C08J 7/16, 5/22					
AU : IPC as above; Australian Classification 47.7-57; 47.7-55						
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>3</sup></b>						
Category <sup>4</sup>	Citation of Document, <sup>5</sup> with indication, where appropriate, of the relevant passages <sup>6</sup>	Relevant to Claim No. <sup>7</sup>				
X	GB,A,896740 (AMERICAN MACHINE & FOUNDRY CO) 16 May 1962 (16.05.62)	(1-35)				
X	AU,B, 67789/60 (254681) (NEDERLANDSE ORGANISATIE VOOR TOEGEPAST-NATUURWETEN SCHAPPELIJK) 24 January 1963 (24.01.63)	(1-35)				
X	Patent Abstracts of Japan, C-411, page 154, JP,A, 61-245803 (TOKUYAMA SODA CO LTD) 1 November 1986 (01.11.86)	(1-35)				
X	AU,B, 47521/64 (290547) (AMERICAN MACHINE & FOUNDRY CO) 20 August 1964 (20.08.64) See page 6 and examples 8-14.	(1-35)				
X	GB,A, 872218 (AMERICAN MACHINE & FOUNDRY CO) 5 July 1961 (05.07.61)	(1-35)				
X	AU,B, 49141/59 (240666) (AMERICAN MACHINE & FOUNDRY CO) 26 November 1959 (26.11.59)	(19,28)				
<div style="display: flex; justify-content: space-between; font-size: x-small;"> <div style="width: 45%;"> <p><sup>8</sup> Special categories of cited documents: (a)</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>						
<b>IV. CERTIFICATION</b>						
Date of the Actual Completion of the International Search <div style="text-align: center; font-family: monospace;">5 October 1988 (05.10.88)</div>		Date of Mailing of this International Search Report <div style="text-align: center; font-family: monospace;">21 OCTOBER 1988 (21.10.88)</div>				
International Searching Authority <div style="text-align: center; font-family: monospace;">Australian Patent Office</div>		Signature of Authorizing Officer <div style="text-align: center;">               D.J. SHEPHERD         </div>				

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